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THE CONTROL OF INSOLUBLE MAGNESIUM COM-POUNDS RESULTING FROM SEA WATER BATTERY OPERATION

Carl E. Mueller, et al

Naval Ordnance Laboratories White Oak, Maryland

December 1967

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THE CONTROL OF INSOLUBLE MAGNESIUM COMPOUNDS RESULTING FROM SEA WATER BATTERY OPERATION

Prepared by: C. E. Mueller and F. M. Bowers

ABSTRACT: The capacity of low rate multicell silver chloride/ magnesium sea water batteries is often limited by a flocculent precipitate that clogs the inlet ports and fills the space between the electrodes. The results of this investigation show that the flocculent precipitate is formed only when magnesium ions (Mg++) are initially present in the electrolyte solution. In magnesium free salt solutions, with a salinity equal to sea water, the precipitate is granular. The magnesium-ion effect can be controlled by passing the incoming sea water electrolyte through a filter of thallous fluoride (TIF) or disodium ethylenediaminetetrascetate (disodium EDTA). The magnesium ions in the sea water electrolyte apparently react with the TIF to form a granular precipitate, and with discdium EDTA to form a soluble magnesium complex. Batteries containing filters of these types were discharged in 3.5% salinity sea water and showed capacity increases ranging from 12 to 60 percent over batteries having no filter. With TIF filters the capacity increase was typically 12 percent and with disodium EDTA the increase was typically 45 percent.

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White Oak, Silver Spring, Maryland

18 December 1967

THE CONTROL OF INSOLUBLE MAGNESIUM COMPOUNDS RESULTING FROM SEA WATER BATTERY OPERATION

This report describes the development of a chemical filter which improves the capacity of silver chloride/magnesium sea water batteries by controlling the formation of precipitates that clog this type of battery during discharge. A patent application has been made for the invention.

The work conducted during this investigation was performed under Task No. MAT 03L 000/F008 98 01 Problem 019.

E. F. SCHREITER Captain, USN Commander

ALBERT LIGHTBODY By direction

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INTRODUCTION

During the development of a low rate multicell silver chloride/
magnesium sea water battery for a sonobuoy application, it was
observed that a flocculent corrosion product would form during
discharge in sea water. This product would gradually clog the 0.070
inch diameter entry ports in those cells nearest the negative
terminal of the battery, and fill the 0.020 inch wide space between
the electrodes in these cells. This condition, often encountered
in commercial sea water batteries, limited the capacity of these
batteries to less than half that theoretically available. When this
battery was discharged in a sodium chloride solution, a granular
corrosion product was formed. The normal flow of solution through
the battery during discharge, flushed this granular precipitate from
the cells. Consequently, the capacity of batteries discharged in
sodium chloride solution was greater than those discharged in sea
water.

The objective of this investigation was to eliminate the clogging of these multicell sea water batteries and thereby improve their capacity. The investigation was divided into two parts: (1) the determination of the cause of the flocculent corrosion precipitate, and (2) its control. This report describes the experiments that were conducted and discusses the effects of various solution parameters.

EXPERIMENTAL APPARATUS AND PROCEDURE

The experimental battery model used in 'he first part of this investigation is shown in Figures 1 and 2. It consisted of a cylindrical lucite block on each end of which was cemented a cell containing an AZ-61 magnesium alloy electrode. AZ-61 magnesium is the alloy commonly used for anodes in silver chloride/magnesium sea water batteries. The configuration of the experimental model was similar to that of Battery WOX-74, a 10 cell silver chloride/ magnesium sea water battery that was developed at the Naval Ordnance Laboratory, White Oak as a power source for sonobuoys. immersing this model in an aqueous salt solution with a dc voltage of 15.2 volts impressed across the electrodes, a condition simulating the parabitic drain (see Discussion) during a 150 ma discharge of Battery WOX-74 was achieved. When the do source was applied. magnesium plated away from the positive electrode and formed a white insoluble precipitate at the negative end. Electrolytic corrosion experiments, of this type, were conducted in Gulf Stream sea water and in other aqueous salt solutions of equal salinity (3.5%). salt solutions contained varying proportions of sodium chloride (NaCl), magnesium chloride (MgCl,), sodium sulfate (NaSO,), and magnesium sulfate (MgSO4). The ions contained in aqueous solutions of these salts represented the four major ions found in sea water which are Nat, Mg T, Cl, and SC, The specific composition of each electrolyte used is given in Table 1.

Experimental runs were usually of three hour duration, but some exploratory experiments were allowed to run for seven hours. Before the start of each expariment, the pH of the electrolyte was measured and adjusted if necessary to pH = 8.254.05, a value equivalent to that of Gulf Stream sea water. Electrolyte pH was also determined upon completion of each experiment. The experiments were conducted at room temperature (22±1°C), and the volume of electrolyte used for each run was usually 1800 ml. The electrical conductivity of the prepared electrolyte solutions was approximately equal to that of sea water as the salinity of all solutions was nearly identical. The specific resistivity of 3.5% salinity sea water is 8 ohm-inchec at 20°C.1,2,2 The precipitate obtained from each experiment was collected and analyzed by x-ray diffraction spectra. A variable resistor was used to maintain a constant voltage of 15 volts between the positive and negative electrodes, and a milliammeter was used to measure the parasitic drain. A schematic diagram of the circuitry used in these experiments is shown in Figure 3.

DISCUSSION OF THEORY AND RESULTS

The dissolution of magnesium anodes in silver chloride/magnesium sea water batteries is directly proportional to both the energy producing reaction and to the anodic corrosion of magnesium. The anodic corrosion rate in multicell sea water batteries, is basically controlled by the parasitic drain. When a number of series connected cells are immersed in a single continuous electrolyte, as is the case with sea water batteries during operation, each cell is shorted to every other cell by means of the connecting conductive sea water. As a result, current flows between points of different potential, flowing outward into the common electrolyte from all the cells in the positive half of the battery and back into the cells of the negative half. This current is referred to as the parasitic drain. complete the circuit, the parasitic drain passes internally through the battery from the negative end to the positive end in addition to the current passing in the same direction to supply the external circuit. A schematic circuit diagram of parasitic current pathways in a multicell sea water battery is shown in Figure 4.

The magnitude of the parasitic drain is dependent on the operating cell voltage, the number of cells, the area and number of inlet and outlet ports to each cell, the length of the ports from the inside of the cell to the common body of electrolyte, and the temperature and salinity of the electrolyte. Reference (4) presents an equation which may be used to calculate the parasitic drain.

$$I_{\text{max}} = EN^2/2b \tag{1}$$

where

I = parasitic drain in amperes

E = operating cell voltage

2N - number of cells per battery

b = CL/KA = resistance of the electrolyte path in ohms

C = specific resistivity of sea water in ohm-inches

L = length of path of sea water from inside the cell to the larger body of the electrolyte in inches

K = number of port holes per cell

A = area of port holes in square inches

This equation shows that reducing the number of cells (2N) per battery, and decreasing the diameter of the entry and exit ports are two ways of reducing the parasitic drain. Figure 5 contains a family of curves showing the parasitic drains, calculated from equation (1), for sea water batteries with five to eleven cells when gas bubbles block-off from 10-70% of the outlet port area at any given time. For the calculations in Figure 5, the diameter of the outlet and inlet ports was taken as 0.070 inch.

The simulated parasitic drain was measured during each experimental run, and the data listed in Table 2 shows that its maximum value varied only slightly with the chemical composition of the electrolyte solution used. This result was not unexpected as the total salt content of each electrolyte solution was constant although the composition varied. The parasitic drain generated with the experimental battery model was usually in the range of 47 to 65 as is shown in Table 2. These values are in good agreement with the calculated value of 60 ma (see Appendix A) obtained from equation (1) for a 10 cell sea water battery with an operating cell voltage of 1.50 volts, with cathodic inlet and outlet port diameters of 0.070 inch, and anodic inlet and outlet port diameters of 0.035 inch and 0.070 inch respectively. These conditions are similar to those used with the experimental model. It is important to note that the value of 60 ms obtained from equation (1) is the maximum parasitic drain one would expect from a sea water battery with the listed parameters. At any given time, however, the parasitic drain is reduced by the presence of gas bubbles in the exit and entry ports of the battery as is shown in Figure 5. This is why a range of values was obtained for the parasitic drain with the experimental battery model.

Another effect of the parasitic drain is that the magnesium at the positive end of the battery acts as an anode, goes into solution and is plated out at the negative side as magnesium hydroxide, an insoluble precipitate. According to Paraday's law which states that one gram equivalent weight of matter is chemically altered at each electrode for every 96,500 coulombs of electricity passed through the electrolyte, the amount of magnesium deplated is directly proportional to the magnitude of the parasitic drain. The electrolytic corrosion of the magnesium anode may be described by the following equation:

$$M_{\rm S} - M_{\rm S}^{++} + 2e^{-}$$
 (2)

When the voltage of the parasitic drain is love the decomposition potential of the sea water electrolyte, a concentration of hydroxylions (0H⁻) occurs about the negative portion of the battery. Since the divalent magnesium ions (Mg⁺⁺) resulting from the electrolytic corrosion of the anodic magnesium migrate to the negative side of the

battery, they react with CHT ions to form an insoluble hydroxide precipitate. The reaction mechanism postulated for the formation of the hydroxy compound is described by the following equations:

$$Mg^{++} + OH^{-} = Mg(OH)^{+}$$
(3)

$$Mg(OH)^{+} + OH^{-} = Mg(OH)_{2}$$
 (4)

The stability of the intermediate product is determined by its stability constant (K) which is equal to the ratio of the $Mg(OH)^+$ ion in equilibrium with the Mg^{++} and the OH^- ion. The greater the value of K_2 the greater the stability of $Mg(OH)^+$. The above reactions are thought reachble since the value of K for reaction (3) is quite high (approximately 380). Although other species may actually be present, x-ray analyses have shown that magnesium hydroxide $[Mg(OH)_2]$ is formed as the primary corresion product.

It was observed that when a low rate multicell silver chloride/
magnesium sea water battery was discharged in sea water, a flocculent
hydroxide precipitate was formed and clogged the inlet ports of the
more negative cells of the battery. The flocculent precipitate also
filled the spaces between the electrodes of these cells. Hence, the
cells became electrolyte starved and battery capacity was significantly
reduced. When the same type of battery was discharged in a sodium
chloride solution of equal salinity, a granular precipitate was
formed. The granular precipitate did not affect battery capacity as
it was easily flushed from the cells during battery discharge.

To determine the cause for the formation of the flocculent hydroxide precipitate in sea water, electrolytic corrosion experiments were conducted in various aqueous salt solutions as shown in Table 1. The results of these experiments show that the physical characteristics of the hydroxy precipitate varied significantly with the chemical composition of the electrolyte used. For example, it was observed that large flocculent applomerates of the hydroxy precipitate were formed only when the divalent Mg " cations were initially present in the electrolyte solution (1.2., solutions B,D.F,G and H of Table 1). This precipitate, in a short time, would clog the inlet port of the newarive cell of the experimental model and restrict the flow of However, in electrolyte solutions initially containing electrolyte. no Mg++ ions (i.e., solutions A.C and E of Tatle 1) a granular precipitate was formed. This precipitate did not clog the negative cell and was easily flushed out into the surrounding body of electrolyta.

The precipitates obtained from each experimental run were analyzed by x-ray diffraction apectra. The spectrum of the precipitates collected from solutions A,B,D,E,F and G (see Table 1) had only one readily identifiable component, Mx(OH)2. In addition, there were two unidentified constituents found in these samples. It is likely that one of these materials was free magnesium, for spalling occurred at the magnesium arode and metal was visible in the corresion products.

The other was either a high molecular weight compound or a material consisting of very small crystals. The chemical composition of this material is not known. The precipitate from solution C was identified as being M; metal. However, it is possible that the concentration of this material was high enough to mask out the Mg(OH), and other constituents present. The spectrum of the precipicate obtained from solution H (sea water) had only one readily identifiable component, calcium carbonate (CaCO₃). There were also some other materials present, but these were not identified as they were marked by the CaCO₃.

Since information available from the x-ray differences in final ph of these salt solutions, Mg+* ions were initially present.

Since the flooculent hydroxy precipitate was formed only khen Mg++ ions were initially present in the electrolyte solution, ways of controlling this ion were also investigated. One approach that was studied was the use of a chemical filter which would remove the Mg** ions from the incoming electrolyte, either by precipitation in a non-flocoulent form or by the formation of a soluble magnesium complex. This phase of the investigation was initiated by studying the feasibility of using theilous fluoride (TIF) to react with the My++ ions in sea water to form a granular precipitate. Thallous fluoride is a white powdery compound that exhibits appreciable requeous solubility. It was possulated that in solution the Mg** lone would reast with the fluoride ions to form a grenular precipitate of management Thursde (MgPs). The thallium lone (Tl* in solution would then react with ONT long to fors thallous hydroxide (TIOA). a strong soluble base. These resulions are described by the following equations:

The thallium ions might also react with other anions in sea water to form additional insoluble salts (i.e., TlC1).

To test this hypothesis, electrolytic corrosion experiments were conducted in sea water and in a manner similar to those described previously. In these experiments, the TIF powder was compressed into a cylindrical pill 1.03 cm long and 0.95 cm in diameter. The pill was wrapped with clear cellophane to prevent the outer surface from dissolving. Through the center of the pill, a 0.18 cm diameter hole was drilled. The pill was then glued over the inlet port of the negative cell of the experimental battery model so that the sea water electrolyte had to pass through the TIF pill before entering the cell. During these experiments only small amounts of the flocculent hydroxy precipitate were formed even though some experiments were allowed to run for as long as seven hours. The resulting precipitates were collected and analyzed by X-ray diffraction spectra. However, no conclusive evidence for the proposed mechanism was obtained as the X-ray diffraction analysis of the precipitates was not definitive.

Other experiments were conducted in which a TIF filter was used during the discharge of actual silver chloride/magnesium sea water batteries (i.e., Battery WOX-74 in sea water). The filters used in these experiments were large enough to encompass the inlet ports of the five cells nearest the negative terminal of the battery. Thus, the sea water electrolyte had to pass through the filter to enter these cells. The TIF filter was fabricated by compressing the powder into the configuration shown in Figure 6, and gluing the formed block into a four-sided lucite case. Hence, the sea water electrolyte came in direct contact with the TIF before entering the five most negative cells. These experiments demonstrated that TIF was capable of controlling the physical characteristics of the insoluble corrosion precipitate formed during battery operation, thereby improving the capacity and operational characteristics of sea water batteries. When compared to control discharges in which the TIF was not used, an average increase of 12% in battery capacity was obtained. Figure 7 shows that the voltage-time characteristics were also improved, for the plateau voltage was extended by a time interval proportional to the percentage increase in capacity.

Whereas TlF can react with the Mg++ ions in sea water to form a granular precipitate (MgFg), it was postulated that disodium ethylene-diaminetetrascetate (disodium EDTA) could react with Mg++ ions to form a solutle magnesium complex. Disodium EDTA is a white crystalline compound, occurring with two molecules of water of hydration. It is represented by the abbreviated formula, Na2HgY*2HgO. This salt is moderately soluble in water. A O.1 M solution has a pH of approximately 5 and behaves as a weak acid. In aqueous solution, the HgY* ion is the complex forming substance and reacts with cations according to the following equation:

$$Me^{+n} + H_2Y^2 = MeY^{(n-1)} + 2H^+$$
 (8)

where n ranges from 2 to 4, one gram-ion of the complex forming ion in all cases reacts with one gram-ion of the metal without regard to its valence. In each case, two gram-ions of the hydrogen ion are also formed. The resulting complexes have the same composition, but differ from one another in the charge they carry. These complexes have been assigned the following structures by Schwarzenbach:

The complexes of the divalent metal ions occur as complex anions, such as Mey. The stability of the complex is characterized by its stability or formation constant (K). This constant defines the ratio of the complex metal ion [Mey(n-4)] in equilibrium with the metal ion (Me+n) in solution. Consequently, the greater the value of K, the greater the stability of the metal complex. In sea water there are two metal ions, calcium (Ca++) and magnesium (Mg++), that will compete to form the Mey complex. However, in sea water the ionic strength of calcium (Ca++) is considerably less (about one-third) than the ionic strength of magnesium (Mg++). Therefore, it was postulated that the magnesium complex of Mgy would form in sea water and thereby control the magnesium ion effect.

To study this hypothesis, electrolytic corrosion experiments were conducted in sea water in a manner similar to that previously described (see Experimental Section). In these experiments, a small quantity of disodium EDTA was wrapped in thin non-woven dynel paper and suspended near the inlet port of the negative cell of an experimental battery model undergoing electrolysis. This approach was used because disodium EDTA could not be compressed into a usable configuration. These corrosion experiments demonstrated that disodium EDTA would be useful in impeding the formation of the floculent type precipitate. However, no conclusive evidence was obtained for the proposed mechanism.

Other experiments were conducted in which disodium EDTA filters were used during the discharge of actual silver chloride/magnesium sea water batteries. The disodium EDTA filters used in these experiments were similar in design to the TlF filter shown in Figure 6. However, since disodium EDTA could not be compressed, the loose crystalline salt was placed within a lucite case and a dynel-webril paper of 0.001 inch thickness was used to enclose the loose salt within the case. Thus, the disodium EDTA was physically contained, but the ions were free to migrate through the thin paper and react with the Mg++ ions in the sea water electrolyte prior to its entering the five most negative cells. The data obtained from these experiments indicate that the capacity of these batteries was significantly increased, and that only a very little of the flocculent type precipitate was formed during battery discharge. When compared to data of control discharges in which neither the TlF or disodium EDTA was used,

an average improvement of 45% in battery capacity was obtained. Figure 8 shows that the time interval of the plateau voltage (useful working voltage) was also increased significantly. These improvements are attributed to the H₂Y^{*} ion which apparently reacted with the Mg*+ ions in sea water to form the soluble complex MgY^{*}, and thereby helped to impede the formation of the flocculent corrosion precipitate.

Figure 9 shows the comparative effect of TIF and disodium EDTA on the capacity and operational characteristics of sea water Batery WOX-74 when discharged at a constant current of 150 ma. Significant improvements in the capacity and operational characteristics of multicell silver chloride/magnesium sea water sonobuoy batteries are achieved by using a chemical filter of the type previously described, especially when disodium EDTA is used as the chemical reagent. Although the control of Mg(CH)s formation in sea water batteries for torpedoes was not studied as a part of this investigation, a suitable disodium EDTA filter might be beneficial when the sea water is recirculated to improve battery operation under conditions of low salinity and low temperature.

CONCLUSIONS AND RECOMMENDATIONS

The inefficiency of low rate multicell silver chloride/magnesium sea water batteries is due to the flocculent corrosion precipitate that forms during battery operation. The flocculent precipitate forms only when magnesium ions (Mg++) are initially present in the sea water electrolyte. This magnesium ion effect is controlled by passing the incoming sea water through a chemical filter during battery operation. At the present time, disodium ethylenediaminetetraacetate (disodium EDTA) is the most effective filter reagent. Batteries containing a filter of this type showed a 45% increase in capacity over those without filters.

It is recommended that this study be continued to determine the actual reaction mechanisms involved. It is also suggested that a chemical filter, such as described in this report, might be used to improve other types of sea water batteries.

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The authors wish to thank Dr. G. Atkinson and Mr. R. Jacobs for their assistance in the development of a chemical filter for controlling the ph.sical characteristics of the insoluble corrosion product formed during sea water battery operation.

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APPENDIX A

Sample Calculation of Parasitic Current.

I_{max} = EN²/2b = the maximum parasitic drain in amperes

E = operating cell voltage = 1.50 volts 2N = number of cells per battery = 10 N² = (10/2) = 25 b = CL/KA = resistance in ohms

C = specific resistivity of sea water = 8 ohm inches at 3.5% salinity and 20°C

L = length of electrolyte path from inside the cell to the larger body of electrolyte = 0.1875 inch

K = number of port holes per cell = 2

A = cross sectional port area in square inches =

D = diameter of port holes

From the above, we get the following:

 $EN^{2} = (1.5)(25) = 37.5$

b = CL/KA = (8) (0.1875)/KA = 1.500/KA

 $KA = \pi r_1^2 + \pi r_2^2$

 $= \pi [(0.035)^2 + (0.0175)^3]$

= 0.481 x 10⁻⁸ square inch

 $b = 1.500/0.481 \times 10^{-9} = 312 \text{ ohms}$

 $I_{max} = 37.5/2(312) = 60 \text{ ma}$

NOTE: This is the maximum leakage current one would expect for a sea water battery with the above parameters. However, at any given instant this value may be reduced as the resistance, b, is significantly increased by the presence of gas bubbles in the exit and entry ports of the battery.

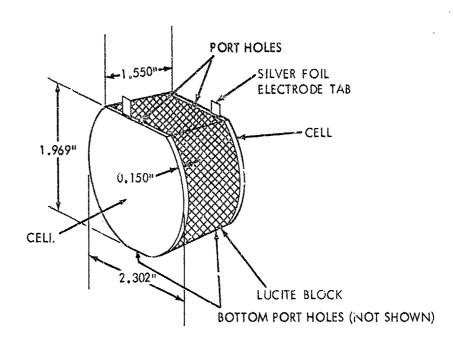


FIG. 1 EXPERIMENTAL BATTERY MODEL

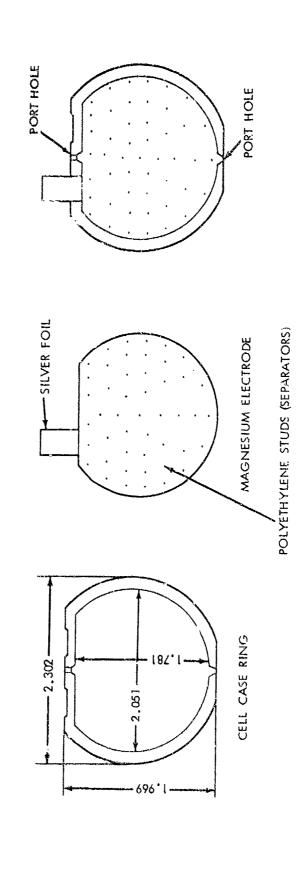
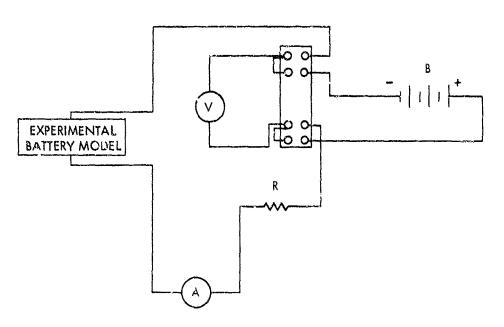


FIG. 2 CELL AND ELECTRODE CONFIGURATION OF EXPERIMENTAL BATTERY MODEL



WHERE.

B = D.C.-IMPRESSED VOLTAGE SOURCE

V = VOLTMETER

R = VARIABLE RESISTANCE A = MILLIAMMETER

FIG. 3 EXPERIMENTAL APPARATUS AND CIRCUITRY

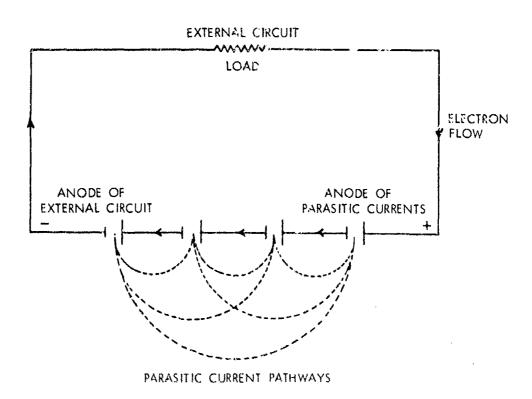


FIG. 4 PARASITIC CURRENT PATHWAYS IN A MULTICELL SEA WATER BATTERY

RESISTANCE IN OHMS

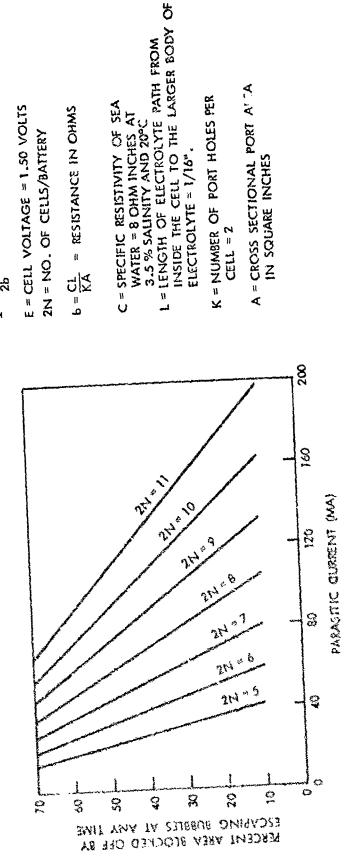
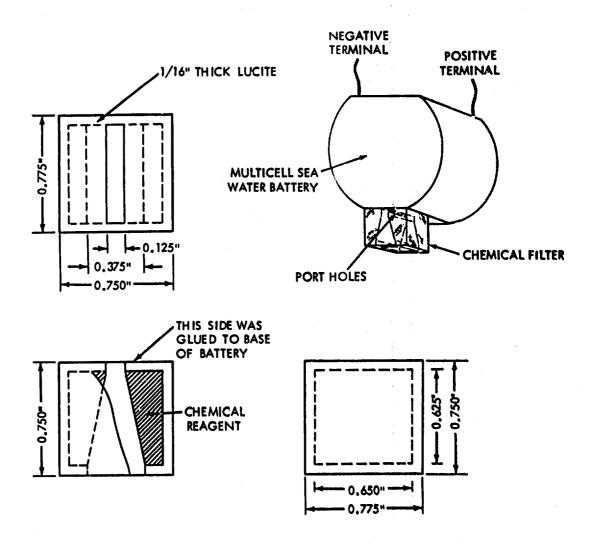


FIG. S VARIABILITY OF PARASITIC CURRENTS IN MILTICELL SEA WATER BATTERIES



NOTE: SCALE 1:2

FIG. 6 CONFIGURATION OF CHEMICAL FILTER

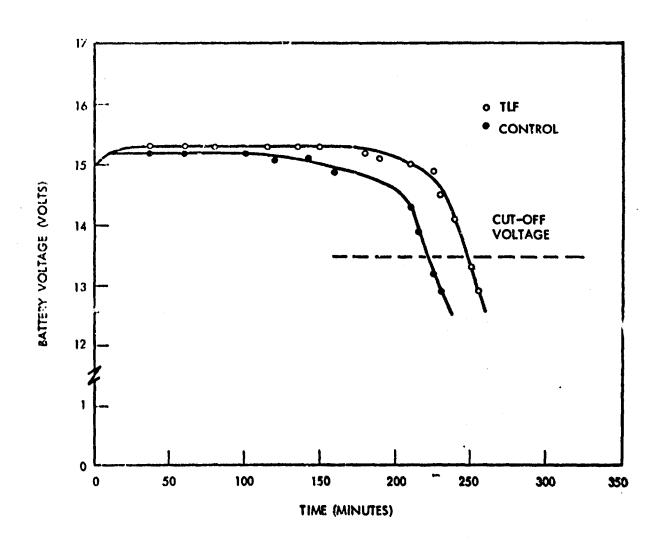


FIG. 7 THE EFFECT OF THALLOUS FLUORIDE (TLF) ON THE CAPACITY OF SEA WATER BATTERY WOX-74 WHEN DISCHARGED AT A CONSTANT CURRENT OF 150 ma.

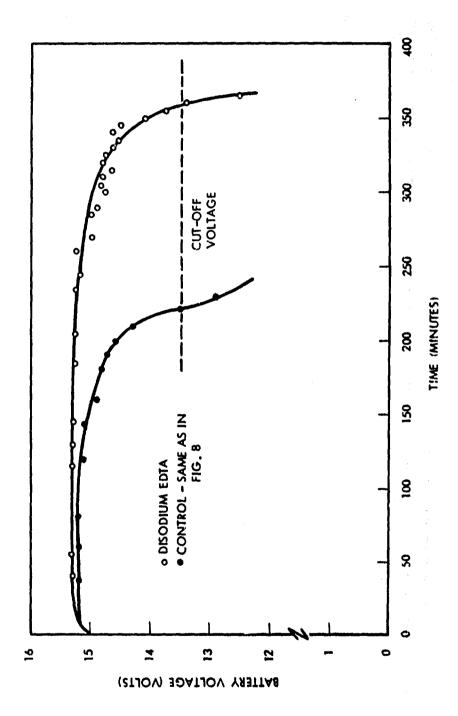


FIG. 8 THE EFFECT OF DISODIUM ETHYLENEDIAMINETETRAACETATE DISODIUM EDTANON THE CAPACITY OF SEA WATER BATTERY WOX-74 WHEN DISCHARGED AT A CONSTANT CURRENT OF 150 mg.

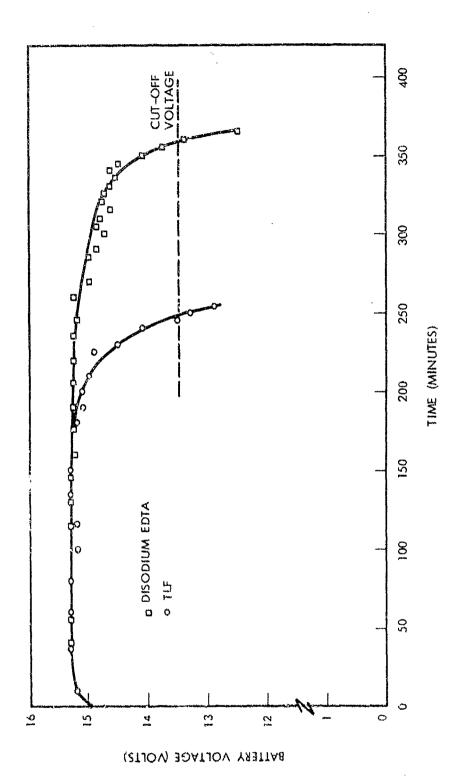


FIG. 9 THE COMPARATIVE EFFECT OF TLF AND DISODIUM EDTA ON THE CAPACITY OF SEA WATER BATTERY WOX-74 WHEN DISCHARGED AT A CONSTANT CURRENT OF 150 ma.

NOLTR 67-120

electroly Solution		ELECTROLYTE COMPOSITION- 3.5% by weight:	Major Ions Present	ph initial ph final
A		NaCl	Na+,C1~	8.30
В		MgCls	Mg++,C1~	9.05
C		N22 SO4	Na ⁺ ,SO ₄ =	8.25
D		MgSO4	Mg*+,SO ₃ =	8.25
E	32/:	39 NaCl & 7/39 Na ₂ SO ₄	Na ⁺ ,C1 ⁻ ,SO ₄ =	8.25
F	32/3	39 NaCl & 7/39 MgSO.	Na+, Mg++ C1=,504 =	9,90
G	32/:	39 NaCl & 7/39 MgCl.	Na+, Mg++ C1-,	9.80
Н		Gulf Stream Sea Water	Na ⁺ , Mg ⁺⁺ , Ca ⁺⁺ C1 ⁻ , SO ₄ **	8.30 9.65

TABLE 1. IDENTIFICATION OF ELECTROLYTE SOLUTIONS

NOLTR 67-120

ELECTROLYTE SOLUTION	TIME of ELECTROLYSIS (hrs)	MAXIMUM SIMULATED PARASITIC CURRENT (ma)	Characteristics Of Insoluble Precipitate
A	2 . 70	55	White Granular Type
В	2.50	47	White, Large Flocculent Agglomerates
С	3.05	50	White Granular Type
D	2.35	47	White, Large Flocculent Agglomerates
E	3.00	52	White Granular Type
F	3.00	65	White, Large Flocculent Agglomerates
G	3.00	50	White, Large Flocculent Agglomerates
H	3.00	65	White, Large Flocculent Agglomerates

TABLE 2. SUMMARY OF ELECTROLYTIC CORROSION DATA